

Determination of Alkalinity (Carbonate and Bicarbonate Hardness)

Introduction

The alkalinity of water is a measure of its capacity to neutralize acids. The alkalinity of natural water is due to the salts of carbonate, bicarbonate, borates, silicates and phosphates along with the hydroxyl ions in free state. However, the major portion of the alkalinity in natural waters is caused by hydroxide, carbonate and bicarbonates. Alkalinity values provide guidance in applying proper doses of chemicals in water and wastewater treatment processes, particularly in coagulation and softening.

The alkalinity of water (also referred to as “p value” and “m value” or acid consumption) is defined as the consumption of hydronium ions up to pH 8.3 and pH 4.5. Results are most commonly expressed as mg/L CaCO₃.

The Alkalinity method is stored as a default method inside the TitroLine® 5000, 7000, 7750, and 7800.

Apparatus

- TL 5000/TL 7000/TL 7750/TL 7800
- Magnetic stirrer
(TM 235 for TL 7000/TL 7750; TM 50 for TL 5000)
- 20 mL exchangeable unit (WA 20) with brown glass bottle for titrant if using TL 7000/TL 7750/TL 7800

Electrode and Electrolyte

- pH combination electrode with integrated temperature sensor, such as A 162 2M-DIN-ID (item # 285130275)
- KCl 3 mol/L electrolyte

Solutions

- **Titrant:** H₂SO₄ or HCl 0.01 - 0.1 mol/L
- **Titer:** Possible with TRIS (Tris (hydroxymethyl)-aminomethan)
- **Calibration solutions:** Technical buffer pH = 4.00 and pH = 7.00 or in DIN buffer pH = 4.01 and pH = 6.87



Calibration

The pH combination electrode is calibrated in technical buffer pH = 4.00 and pH = 7.00 or in DIN buffer pH = 4.01 and pH = 6.87.

Example of the calibration documentation

Calibration

Buffers used

pH buffer 1:	TEC_4.000
pH buffer 2:	TEC_7.000

Measured values

pH buffer 1:	TEC_4.000	165.6 mV / 23.4 °C
pH buffer 2:	TEC_7.000	-11.2 mV / 23.0 °C

Calibration data

Slope:	99.4 % / -58.8 mV/pH
Zero point:	pH 6.81 / -11.2 mV
Temperature:	23.4 °C (a)
Date and time:	07.03.13 / 15:04

Determination of the exact concentration of the titrant (optional)

The exact concentration of the titrant can be determined using a titrimetric standard TRIS (hydroxymethyl)-aminomethan. TRIS is dried in a desiccator overnight at room temperature before the titer determination is carried out.

The standard method for HCl/H₂SO₄ titrant (titer HCl) is stored as a default method inside the TitroLine® 5000/7000/7750/7800 titrators.

The factor 1 (F1) should be changed to 2 if titrant 0.05 mol/L H₂SO₄ is used.

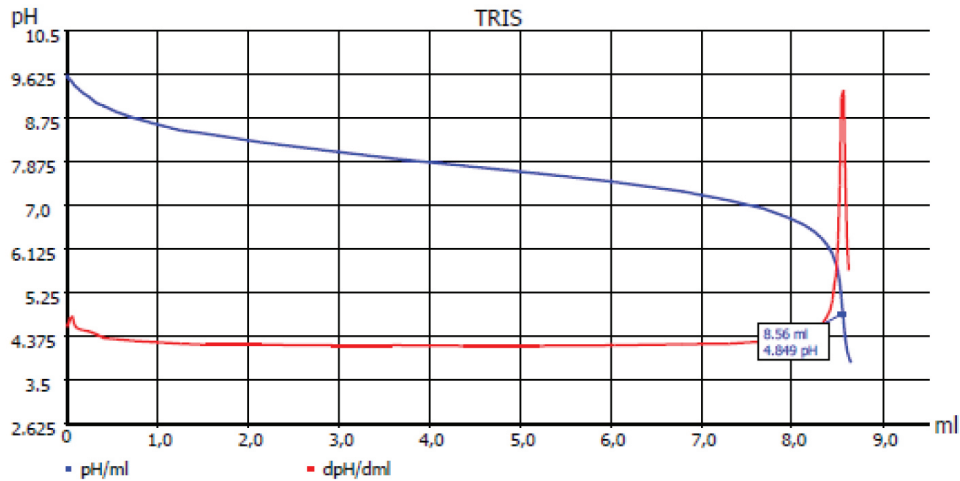
Factor 2 (F2):	1000.0000
Factor 1 (F1):	1.0000

In a 100 or 150 mL beaker, 0.2 to 0.3 g TRIS primary standard is weighed accurately and dissolved in 60 to 80 mL of distilled water with stirring.

Documentation example for standard titration of H₂SO₄/HCl with TRIS:

GLP documentation

Titration graph



Method data

Method name:	Titre HCl	Titration duration:	3 m 8 s
End date:	13.09.12	End time:	14:39:30

Titration data

Sample ID:	TRIS	Weight:	0.1038 g
Start pH:	pH 9.590	End pH:	pH 3.864
Start temperature:	25.0 °C (m)	End Temperature:	25.0 °C (m)
Zero point:	pH 6.83 / -10.0 mV	Slope:	100.6 % / -59.5 mV/pH
EQ:	8.560 ml / pH 4.849	Titre:	0.1001 mol/l

Calculation formula

Titre:	$(W \cdot F2) / ((EQ1 - B) \cdot M \cdot F1) \rightarrow M103$
Mol (M):	121.14000

Weight (W):	Man	Factor 2 (F2):	1000.0000
Blank value (B):	0.0000 ml	Factor 1 (F1):	1.0000
Statistics:	Off		

Method for standard titration of H₂SO₄/HCl with TRIS

Method data overall view

Method name:	Titer HCl	Created at:	09/13/12 14:23:02
Method type:	Automatic titration	Last modification:	09/13/12 14:27:56
Measured value:	pH	Damping settings:	None
Titration mode:	Dynamic	Documentation:	GLP

Dynamic: Steep

Measuring speed / drift	Normal:	Minimum holding time:	02 s
		Maximum holding time:	15 s
		Measuring time:	02 s
		Drift:	20 mV/min

Initial waiting time:	0s		
Titration direction:	Decrease		
Pretitration:	Off		
End value:	2.500 pH		
EQ:	On (1)		
Slope value:	Steep	Value:	700

Dosing parameter

Dosing speed:	100.00 %	Filling speed:	30 s
Maximum dosing volume:	50.00 ml		

Unit values

Unit size:	20 ml
Unit ID:	10039005
Reagent:	HCl 0.1 mol/L
Batch ID:	No Charge
Concentration [mol/l]:	0.10070
Determined at:	12/05/11 19:18:45
Expire date:	08/18/12
Opened/compounded:	09/10/11
Test according ISO 8655:	05/10/11
Last modification:	09/13/12 14:35:18

Device information

Device:	TitroLine 7000
Serial number:	00012
Software version:	1230

Titre_HCl_13_09_12-14_36_21.pdf

Titration of the sample

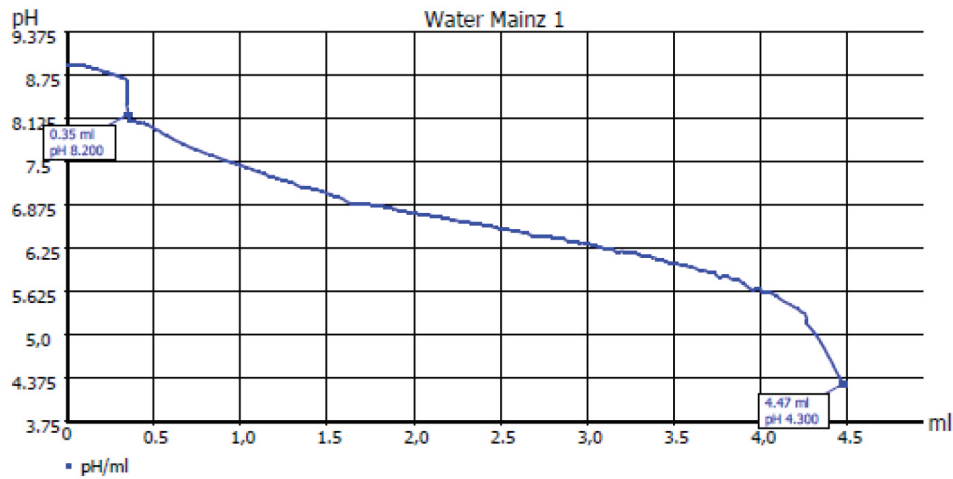
Load the default method "Alkalinity". The method is ready to use.

A 100 mL water sample is pipetted into a beaker and titrated. If the consumption using HCl 0.1 mol/L is less than 2 mL, the sample should be repeated using HCl 0.02 mol/L. Considering that this titration is an end-point titration, the titrator should be calibrated on a weekly or daily basis.

Result example: p and m-value

GLP documentation

Titration graph



Method data

Method name:	Alkalinity (p+m)	Titration duration:	3 m 17 s
End date:	22.11.12	End time:	15:57:02

Titration data

Start pH:	pH 8.913	Pattern:	100.00000 ml
Start temperature:	21.4 °C (a)	End pH:	pH 4.259
Zero point:	pH 7.00 / 0.0 mV	End temperature:	21.5 °C (a)
EP1:	0.354 ml / pH 8.200	Slope:	100.0 % / -59.2 mV/pH
		p-value:	0.35 mmol/l
EP2:	4.475 ml / pH 4.300	m-value:	4.47 mmol/l

Calculation formula

p-value:	$(EP1-B)*T*M*F1/(V*F2)$	Mol (M):	1.00000
m-value:	$EP2*T*M*F1/(V*F2)$	Mol (M):	1.00000
Blank value (B):	0.0000 ml	Titre (T):	0.10000000 (m)
Factor 1 (F1):	10.0000	Pattern (V):	100.0000 ml (f)
Factor 2 (F2):	0.0100	Statistics:	Off

Method Information

Method data overall view

Method name:	Alkalinity (p+m)	Created at:	11/22/12 15:51:09
Method type:	Automatic titration	Last modification:	11/22/12 15:53:15
Measured value:	pH	Damping settings:	None
Titration mode:	End pt.	Documentation:	GLP
Linear steps:	0.020 ml		

Measuring speed / drift:	Normal:	Minimum holding time	02 s
		Maximum holding time	15 s
		Measuring time:	02 s
		Drift:	20 mV/min

Initial waiting time:	0 s
Titration direction:	Decrease
Pretitration:	Off

Endpoint 1:	pH 8.200	Delta endpoint 1:	pH 0.500
		Endpoint delay 1:	4 s
Endpoint 2:	pH 4.300	Delta endpoint 2:	pH 1.000
		Endpoint delay 2:	10 s

Dosing parameter

Dosing speed:	15 %	Filling speed:	30 s
Maximum dosing volume:	50.00 ml		

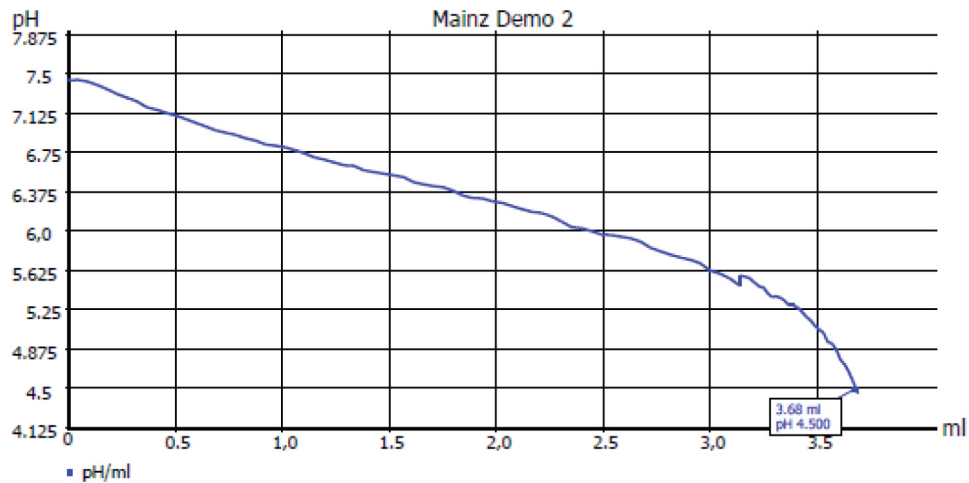
Unit values

Unit size:	20 ml
Unit ID:	10039005
Reagent:	HCl 0.1 mol/L
Batch ID:	no Charge
Concentration [mol/l]:	0.10030
Determined at:	11/22/12 18:14:29
Expire date:	08/18/12
Opened/compounded:	09/10/11
Test according ISO 8655:	05/10/11
Last modification:	11/22/12 10:14:33

Result example: only m-value

GLP documentation

Titration graph



Method data

Method name:	Alkalinity (p+m)	Titration duration:	3 m 6 s
End date:	18.02.14	End time:	16:52:29

Titration data

Sample ID:	Mainz Demo 2	Pattern:	100.000 ml
Start pH:	pH 7.432	End pH:	pH 4.451
Start temperature:	19.4 °C (a)	End temperature:	19.7 °C (a)
Zero point:	pH 6.89 / -6.3 mV	Slope:	98.7 % / -58.4 mV/pH
EP1:	0.000 ml / pH 8.200	p-value:	0.00 mmol/l
EP2:	3.679 ml / pH 4.500	m-value:	3.68 mmol/l

Calculation formula

p-value:	$(EP1-B)*T*M*F1/(V*F2)$	Mol (M):	1.00000
m-value:	$EP2*T*M*F1/(V*F2)$	Mol (M):	1.00000
Blank value (B):	0.0000 ml	Titre (T):	0.10000000 (m)
Factor 1 (F1):	10.0000	Pattern (V):	100.000 ml (f)
Factor 2 (F2):	0.0100	Statistics:	Off



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